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Thermo-chemical routes for hydrogen rich gas from biomass: A review

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Abstract

As the demand of energy is growing faster due to society up gradation and rapid industrialization, renewable energy sources hold promise for the future energy resources in developed and third world developing countries. In contrast to conventional energy sources, non-conventional energy sources like wind, sunlight, water, and biomass have been used as renewable energy sources since ancient times. Worldwide research and energy policy are focusing towards the hydrogen economy. Hydrogen is considered as a forecast to become major source of energy in the future. Hydrogen production plays an important role in development of economy. As biomass is abundant, clean and renewable, production of hydrogen from biomass is one of the promising approaches.

Present review article focuses to highlight various thermo-chemical processes for conversion of biomass into hydrogen rich gas. Effect of various parameters such as temperature, catalyst activity and biomass /steam ratio has been discussed in view of gas yield pattern in addition to physicochemical properties of hydrogen and its uses.

Keywords: Hydrogen; Biomass; Thermo-chemical; Gasification

Contents

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1. Introduction

The present status and future predictions indicate that the availability of fossil fuel is not certain for long period. Thus there is an utmost need of a substitute fuel which is obtained preferably from renewable resources and its use environment friendly. The hydrogen has been found to be well suited for this purpose as hydrogen is clean and of high calorific value fuel. Biomass has been considered as one of the most probable source for hydrogen production.

Hydrogen is either manufactured from fossil fuels such as natural gas, naphtha and coal, or from non-fossil energy resources like water electrolysis, photolysis and thermolysis [1–3].

Presently, worldwide research and energy policy is focusing towards the hydrogen economy. Hydrogen is considered as a forecast to become major source of energy in the future. Hydrogen production is likely to play an important role during the development of economy. As biomass is abundant, environment friendly and renewable; the production of hydrogen from biomass is a promising approach. Biomass derived hydrogen is likely to become a fuel of tomorrow.

2. Hydrogen

Cavendish in 1766, while studying the component effects of the dilute acids on metals like Zn, Fe and tin, found that a similar gas was obtained in each case. He called this gas as inflammable air since it burnt when ignited. The name hydrogen (Greek: *Hydru* = water forming) was given to the gas by Lavoisier who found that the gas when burnt in air produced water. Hydrogen with atomic weight 1.00797 and atomic number 1 is the first element in the periodic table having the electronic configuration $1s^1$. Three isotopes of hydrogen viz. $^1H_1$, $^2H_1$ and $^3H_1$ with atomic weight 1, 2 and 3 are known. These are hydrogen, deuterium and tritium, respectively. Hydrogen is a colourless, tasteless and odorless gas. It is the lightest element known with density of 0.0695 with respect to air. It is sparingly soluble in water. Various physical properties of hydrogen are listed in Table 1. The combustion and explosion properties of hydrogen are given in Table 2.

Table 1
Physical properties of hydrogen

	P-Hydrogen	n-Hydrogen
Triple point		
Temperature (K)	13.803	13.957
Pressure (KPa)	7.04	7.2
Density (solid) (kg/m^3)	86.48	86.71
Density (liquid) (kg/m^3)	77.03	77.21
Density (vapor) (kg/m^3)	0.126	0.130
Boiling point (101.3 Kpa) (K)	20.268	20.39
Heat of vaporization (J/mol)	898.30	899.1
Liquid phase		
Density (kg/m^3)	70.78	70.96
C_p (J/mol/K)	19.70	19.7
C_v (J/mol/K)	11.60	11.6
Enthalpy (J mol)	−516.6	548.3
Entropy (J/mol/K)	16.08	34.92
Viscosity (m Pa s)	13.2×10^{-3}	13.3×10^{-3}
Velocity of sound (m/s)	1089	1101
Thermal conductivity (W/m/K)	98.92×10^{-3}	100×10^{-3}
Compressibility factor	0.01712	0.01698
Gaseous phase		
Density (kg/m^3)	1.338	1.331
C_p (J/mol/K)	24.49	24.60
C_v (J/mol/K)	13.10	13.2
Enthalpy (J/mol)	381.61	1447.4
Entropy (J/mol/K)	60.41	78.94
Viscosity (m Pa s)	1.13×10^{-3}	1.11×10^{-3}
Velocity of sound (m/s)	355	357
Thermal conductivity (W/m/K)	60.49×10^{-3}	16.5×10^{-3}
Compressibility factor	0.906	0.906
Critical point		
Temperature (K)	32.976	33.19
Pressure (MPa)	1.29	1.325
Density (kg/m^3)	31.43	30.12
Properties at STP (273.15 K, 101.3 K pa)		
Density (kg/m^3)	0.0899	0.0899
C_p (J/mol/K)	30.35	28.59
C_v (J/mol/K)	21.87	20.3
Viscosity (m Pa s)	8.34×10^{-3}	8.34×10^{-3}
Velocity of sound (m/s)	1246	1246
Thermal conductivity (W/m/K)	182.6×10^{-3}	173.9×10^{-3}
Compressibility factor	1.0005	1.00042
Dielectric constant	1.00027	1.000271
Prandtl number	0.6873	0.680

Table 2
Combustion and explosion properties of hydrogen

Properties	Hydrogen
Density at STP (kg/m^3)	0.084
Heat of vaporization (J/g)	445.6
Lower heating value (kJ/g)	119.93
High heating value (kJ/g)	141.8
Thermal conductivity at std. condition (mW/cm/K)	1.897
Diffusion coefficient in air at std. condition (cm^2 s)	0.61
Flammability limits in air (vol%)	4.0–75
Detonability limits in air (vol%)	18.3–59
Limiting oxygen index (vol%)	5.0
Stoichiometry composition in air (vol%)	29.53
Minimum energy of ignition in air (Mj)	0.02
Auto ignition temperature (K)	858
Flame temperature in air (K)	2318
Maximum burning velocity in air at std. condition (m/s)	3.46
Detonation velocity in air at std. condition (km/s)	1.48–2.15
Energy of explosion mass related g TNT (g)	24.0
Energy of explosion volume related g TNT (m^3) (STP)	2.02

2.1. Uses of hydrogen

Although hydrogen has wide applications, few industrial uses of hydrogen gas are mentioned below [4]:

- In industries as chemical feedstock for production of certain chemicals.
- In the core industries like ammonia manufacturing, petroleum refining and petrochemicals production.
- In food industries for hydrogenation of unsaturated oils of soybeans, fish, cottonseed, corn, peanut and coconut.
- Hydrogenation of inedible oils and greases for manufacturing soaps and animal feed.
- In the production of float glass.
- In oxy-hydrogen cutting of glass.
- In energy storage technology.
- Liquid hydrogen is stored as energy carriers.
- In electronics industry.
- Highly pure hydrogen gas is used for the production and processing of silicon.
- Hydrogen is used as an alloying element in various amorphous materials.
- Hydrogen used as fuel for rocket propulsion.
- In fuel cells.
- In the transportation sector.

3. Biomass

Biomass is the fourth largest source of energy in the world, accounting for about 15% of the world's primary energy consumption and about 38% of the primary energy consumption in developing countries [5]. Biomass consists of all the living material

present on earth. Biomass may vary significantly in its physical and chemical properties due to different variety and diversified origin. Usual composition of biomass comprises cellulose, hemi-cellulose, lignin, extractives and inert ash.

The direct use of biomass to produce heat by combustion is an inefficient way of utilizing its energy and it contributes to enhance environmental pollution. Biomass resources can be divided into two broad categories; natural and derived materials. These categories can be further subdivided as wastes, forest products and energy crops [6]. There is a vital need of a process, which can convert biomass into useful energy products like oil, gases, etc. Pyrolysis and gasification of the waste materials have been found to be the most favourable thermo-chemical conversion processes for utilizing renewable biomass energy.

3.1. Biomass conversion technologies

Biomass can be converted into useful forms of energy products using a number of different processes. Factors that influence the choice of process are the type and quantity of biomass feedstock. Different routes for biomass conversion into hydrogen rich gas are:

(i) Thermo-chemical conversion.
(ii) Bio-chemical/biological conversion.
(iii) Mechanical extraction.

Thermo-chemical conversion processes comprise three different processes as described below [7]:

(i) *Combustion*: The burning of biomass in air, i.e., combustion is worldwide adopted process to obtain a range of outputs like heat, mechanical power or electricity by converting the chemical energy stored in biomass. Combustion of biomass produces hot gases in the temperature range of 800–1000 °C. Combustion is feasible only for biomass having moisture content less than 50%, otherwise the biomass have to be pre-dried [8].

(ii) *Gasification*: Gasification is the conversion of biomass into a combustible gas mixture by the partial oxidation of biomass at high temperatures, typically in the range of 800–900 °C. The low calorific value gas produced can be directly utilized as a fuel for gas turbines and gas engines [8]. Many gasification methods are available for producing fuel gas. Based on throughput, cost, complexity and efficiency issues, circulated fluidized bed gasifiers are suitable for large-scale fuel gas production.

(iii) *Pyrolysis*: Pyrolysis is conversion of biomass to liquid, solid and gaseous fractions by heating the biomass in the absence of air at around 500 °C temperature [8]. In addition to gaseous product, pyrolysis produces a liquid product called bio-oil, which is the basis of several processes for the development of the various energy fuels and chemicals. Pyrolysis reaction is an endothermic reaction as mentioned below:

$$\text{Biomass} + \text{Energy} \rightarrow \text{Bio-oil} + \text{Char} + \text{Gas}.$$

Tijmensen et al. [9] have reviewed the technical feasibility and economics of biomass integrated gasification—Fischer Tropsch process in general, identifying the most promising system configurations and key R&D issues essential for the commercialization of this technology.

4. Technologies for hydrogen production

4.1. Hydrogen formation via supercritical water extraction

By treating biomass in supercritical water, biomass can be converted into fuel gases, which are rich in hydrogen. Water is attractive as a potential medium for industrial chemical reactions because it is environmentally benign. Lot of research work has been carried out in aqueous conversion of whole biomass to hydrogen under low temperature but supercritical conditions.

Calzavara et al. (2004, France) have critically reviewed the biomass gasification in supercritical water process for hydrogen production. Authors have indicated that the key point of the process is energy recovery as the chemical reaction is endothermic and needs high temperature and rather a large ratio of water/biomass [10].

Demirbas (2003, Turkey) has conducted experiments for the production of hydrogen from fruit shells using aqueous conversion process [3]. Author used the shell samples of walnut, sunflower, hazelnut, cotton cocoon and almond for performing experiments of supercritical water extraction (SWE) in a 100 ml cylindrical autoclave with construction material of SS 316. Experiments were carried out at various temperatures viz. 650, 670, 690, 710, 730 and 750 K and at different operating pressures viz. 23, 28, 33, 38, 43 and 48 MPa. The author has suggested that as compared to other thermo-chemical processes like pyrolysis, SWE can directly deal with the wet biomass samples by eliminating the drying process [3].

Results of Tables 3 and 4 indicate that there is an increase in the product yields with increase in temperature and pressure. It can be observed from Table 3 that a maximum gas yields of 66.4%, 64.7%, 63.5%, 65.7% and 61.3% were obtained at a temperature of 750 K, using SWE process for almond, cotton cocoon, hazelnut, sunflower and walnut, respectively. The results of Table 4 indicate that for all type of biomass, maximum gas yield was obtained at a pressure of 48 MPa.

Feng and coworkers have described about the phase equilibrium in two biomass conversion processes viz. hydrothermal upgrading (HTU) process and supercritical water gasification wherein, bio-crude is the main target in HTU and gas is the main product in SWE [11].

The interest of supercritical water, i.e., with temperature and pressure above its critical point ($T > 374\,^{\circ}C$ and $P > 220$ bar) as a reactive medium, is due to its specific transport and

Table 3
Hydrogen yields using SWE process at different temperatures (K)

Temperature (K)	Hydrogen yields (%)				
	Almond	Cotton cocoon	Hazelnut	Sunflower	Walnut
650	54.6	52.4	50.8	53.8	47.9
670	58.5	56.3	54.7	58.0	51.6
690	61.4	59.7	58.0	61.3	55.4
710	63.7	64.0	61.5	62.9	58.3
730	64.5	65.3	62.6	64.7	60.2
750	66.4	67.1	65.1	66.8	62.4

Table 4
Hydrogen yields using SWE process at different pressures (MPa)

Pressure (MPa)	Hydrogen yields (%)				
	Almond	Cotton cocoon	Hazelnut	Sunflower	Walnut
23	54.6	52.4	50.8	53.8	47.9
28	58.8	56.3	54.7	58.0	51.6
33	61.8	59.7	58.0	61.3	55.4
38	64.6	64.0	61.5	62.9	58.3
43	65.7	65.3	62.6	64.7	60.2
48	68.4	67.1	65.1	66.8	62.4

solubilization properties. Supercritical water acts as a homogeneous non-polar solvent having high diffusivity and high transport properties, which is able to dissolve any organic compounds and gases. In such a process, hydrogen can be produced at thermodynamic equilibrium because of operating process conditions.

4.2. *Fast pyrolysis*

Fast pyrolysis is a process in which biomass is converted into liquid, gases and solid products by heating at high temperature in an inert atmosphere. This process is carried out to obtain more of the liquid product in addition to some proportion of gaseous product, containing comparatively lesser amounts of hydrogen.

The product yield pattern of pyrolysis process using biomass is strongly relevant to chemical composition of biomass. Under fast heating and pyrolysis conditions as in the free fall reactor, an interaction of the biomass pyrolysis with the in situ steam reforming of the pyrolysis intermediate products occurs, which leads to more hydrogen rich gas. During pyrolysis, operating parameters such as particle size, temperature, heating rate, residence time, steam/biomass (S/B) ratio and catalyst strongly affect the yield pattern and properties of products.

The authors of the present article are perusing research and development studies on two routes for hydrogen production. First route involves steam reforming of the bio-oil obtained from fast pyrolysis of biomass. For this purpose the author and co-workers are engaged in performing fast pyrolysis of biomass using various parameters. Experiments are under progress using a fixed bed reactor to optimize the product yield pattern. The second route focuses on direct gasification of biomass in the presence of gasifying agent and catalyst. The biomass like *Calotropis Procera*, sugarcane bagasse and *Jatropha Curcus* seed cake are used as feed for these studies.

Columba Di Blasi and coworkers (Italy, 1999) have carried out initial pyrolysis experiments in a countercurrent fixed bed reactor using different biomass viz. beech-wood, nutshells olive husks, grape residues and straw pellets to evaluate the role of de-volatilization stage on the heating value of the producer gas. Table 5 presents the yield patterns of different types of biomass using pyrolysis process indicating that the gas yield is maximum with Straw pellets and minimum with Beech-wood [12].

Table 5
Product yield pattern of different biomass

Biomass	Char (wt%)	Gas (wt%)	Liquids (wt%)
Beech-wood	29.00	16.03	55.54
Nutshells	36.82	17.91	41.66
Olive husks	34.13	19.60	46.01
Grape residues	44.84	17.44	35.72
Straw pellets	34.63	20.10	41.50

4.3. Catalytic pyrolysis/gasification

Pyrolysis is an important process for obtaining energy from biomass. Valuable hydrogen rich gas can also be generated by pyrolysis. There are three methods for producing hydrogen rich gas. Firstly, hydrogen can be produced by steam reforming of pyrolysis liquid obtained from the pyrolysis of biomass. Secondly, the pyrolysis process is carried out around 700 °C and including the removal of tar content of the gas and improving the quality of the product gas. In the second stage catalysts, normally dolomites and Ni, high temperatures, steam and oxygen could be used. In the third option the pyrolysis occurs at a lower temperature (<750 °C) and catalyst is incorporated in the same reactor where the pyrolysis of biomass occurs. Catalytic pyrolysis/gasification is one of the promising options for tar elimination from the product gas [13].

Dolomite and Ni based steam reforming catalysts are the most conventional and active catalysts for tar cracking at 1073–1173 K for dolomite and 973–1073 K for Ni based catalyst. Various types of oxide catalysts were also studied and CeO_2 was found to be a better option. It was incorporated as $Rh/CeO_2/SiO_2$ catalyst. In case of cedar wood biomass, 98% conversion into gaseous product was achieved. The gasification of cellulose has been investigated using Rh catalyst supported on CeO_2, ZrO_2, Al_2O_3, TiO_2, MgO and SiO_2 at lower temperatures (723–823 K). Another catalyst $NiAl_2O_4$ was also used for the catalytic gasification of biomass with Ni content of 33%. It is a green crystalline compound with bulk density 1100 kg/m^3. Copper based catalysts can also be used to produce hydrogen by steam reforming of methanol at temperatures above 550 K [14,15].

The catalysts are also compared on the basis of their selectivity for hydrogen production. Silica supported Rh, Ru and Ni show low selectivity for hydrogen production while Pt, Ni and Ru exhibit higher activities for the reforming reaction. Only Pt and Pd show relatively high selectivity for the hydrogen production. Another catalyst, rhodium hydro-calcite ($Mg_4Rh_{0.48}Al_{1.95}O_7$) has been successfully used for the production of syngas by partial oxidation of methane.

Catalyst can be placed into the pyrolysis reactor in two ways, either in the layer of glass wool and otherwise it can be mixed with the original biomass particles prior to the experiments.

Catalytic performance of Rh/CeO_2 in the gasification of cellulose to syngas was studied by Md. Asadullah and coworkers [13]. They investigated the effect of Rh catalysts supported on CeO_2, ZrO_2, Al_2O_3, TiO_2, MgO and SiO_2 at comparatively low temperatures viz. 723–823 K. Experiments were carried out using a laboratory scale fluidized bed reactor using air as the gasifying agent. Among the catalysts, Rh/CeO_2 showed excellent results

with 100% conversion of carbon to gas. Table 6 presents the hydrogen gas yield patterns with different catalysts used by the authors. The maximum hydrogen yield was observed for the catalyst Rh/CeO_2. The results of Table 7 indicate that hydrogen yield increased with the increase in the temperature [13].

Asadullah et al. (Japan, 2002) conducted the catalytic gasification of cedar wood using a highly efficient catalyst Rh/CeO_2/SiO_2(60) catalyst and air as the gasifying medium. Experiments were conducted in a continuous feeding fluidized bed gasifier at temperatures of 823–973 K. It was reported that the Rh catalyst provided much better results as compared with conventional Ni and dolomite catalysts in the carbon conversion to syngas. Table 8 presents the yield patterns with temperature and CeO_2 loading quantity in the catalyst [16].

Dalai and coworkers have carried out systematic studies for the steam gasification of biomass materials such as cedar wood and aspen. They performed experiments using a technique called temperature-programmed gasification and constant temperature gasification. CaO catalyst was studied for this purpose and studies were conducted by varying the catalyst loading (0–4.0 wt%). The results of Table 9 indicate that hydrogen and the total fuel yield increased to some extent with the increase in the CaO loading and later obtained a constant value with further increasing the load for all the biomass types [17].

Table 6
Performance of different catalysts on hydrogen yields

Catalyst type	Hydrogen yields (per μmol)
None	90
CeO	263
MgO	430
TiO_2	560
ZrO_2	490
Al_2O_3	480
SiO_2	230
Rh/CeO_2	1290
Ru/CeO_2	1101
Pd/CeO_2	830
Pt/CeO_2	850
Ni/CeO_2	740
G-917	60
Rh/TiO_2	800
Rh/MgO	820
Rh/SiO_2	720

Table 7
Hydrogen yields at different temperatures

Temperature (K)	H_2 gas yields (μmol)
730	1155
780	1300
830	1320
880	1330

Table 8
Variation in yields with catalyst loading and temperature

Catalyst	Temperature (K)	Formation rate (mmol/min)				H_2/CO	C-conv (%)	Char (%)	Tar (%)
		CO	H_2	CO_2	CH_4				
$Rh/CeO_2/SiO_2$(35)	823	618	1007	1225	71	1.6	83	14	3
	873	901	1298	1145	116	1.4	91	8	1
	923	1141	1360	1005	87	1.2	95	3	2
	973	1387	1535	835	54	1.1	98	2	0
$Rh/CeO_2/SiO_2$(50)	823	530	875	1135	235	1.7	83	11	6
	873	596	1276	1406	110	2.1	92	6	2
	923	835	1210	1174	170	1.5	95	4	1
	973	1083	1350	1003	110	1.3	96	4	0
$Rh/CeO_2/SiO_2$(60)	823	536	883	1155	255	1.7	85	10	5
	873	676	1116	1240	254	1.7	95	5	0
	923	890	1117	1095	272	1.3	98	2	0
	973	945	1207	1097	238	1.3	99	1	0
$Rh/CeO_2/SiO_2$(75)	823	251	834	1257	390	3.3	83	11	6
	873	622	925	1142	335	1.5	92	7	1
	923	715	991	1054	328	1.4	91	5	4
	973	1058	1175	880	267	1.1	96	2	2

Table 9
Hydrogen yields with CaO loading

CaO load (per wt%)	Hydrogen yield (per %)
Cedar wood	
0	48.0
1	54.0
2	57.0
3	61.0
4	61.0
Aspen	
0	45.0
1	47.0
2	49.0
3	51.0
4	54.0

Javier Gill and team members have studied the effects of the in bed use of dolomite under different operating conditions. Tar was successfully reduced to 1 g/m^3 by using 15–30 wt% of dolomite. Experiments were carried out in small-scale pilot plant with equivalent ratios between 0.20 and 0.35 and temperatures of 800–840 °C. The gas yields were found to increase with different ER values (Table 10) [18].

Table 10
Gas yield with different ER values

ER values	Gas yield (m^3, dry gas/kg daf)
0.18	1.8
0.19	1.9
0.21	2.1
0.22	1.9
0.24	2.1
0.26	2.2
0.27	2.2
0.32	2.3
0.37	2.4

4.4. Biomass gasification

Gasification is the conversion of biomass into a combustible gas mixture by the partial oxidation of biomass at high temperatures, typically in the range of 800–900 °C. The process performs partial oxidation to convert carbonaceous feed stock into gaseous energy carrier consisting of permanent, non-condensable gas mixture (CO, CO_2, CH_4, H_2 and H_2O). In an ideal gasification process biomass is converted completely to CO and H_2 although in practice some CO_2, water and other hydrocarbons including methane are formed. Most simple biomass gasifiers produce approximately equal proportions of CO and hydrogen.

The main reaction steps in biomass gasification are [19]:

- Heating and pyrolysis of the biomass whereby converting biomass into gas, char and primary tar.
- Cracking of primary tar to gases and secondary and tertiary tars.
- Cracking of secondary and tertiary tars.
- Heterogeneous gasification reactions of the char formed during pyrolysis and homogeneous gas phase reactions.
- Combustion of char formed during pyrolysis and oxidation of combustible gases.

In a gasification processes, the solid fuels are completely converted (except the ashes in the feed) to gaseous products having different compositions. Because of the production of cleaner gaseous fuel as well as almost complete conversion of biomass, the gasification process for converting biomass into energy is becoming an attractive option. The char produced from the fast pyrolysis of biomass is highly reactive and can be gasified with gasifying agents such as steam, CO_2, oxygen and H_2 to gaseous fuels. Recently, there is a lot of interest in utilizing the pyrolysis derived char for steam gasification to produce gaseous fuel. The oxidation reaction involved is mentioned below:

$$C + O_2 \rightarrow CO_2, \tag{1}$$

$$2(-CH_2) + 3O_2 \rightarrow 2H_2O + 2CO_2. \tag{2}$$

The gasification reactions of organic materials are also mentioned as follows [22]:

$$C + H_2O \rightarrow CO + H_2, \tag{3}$$

$$C + CO_2 \rightarrow 2CO, \tag{4}$$

$$(-CH_2) + H_2O \rightarrow CO + 2H_2, \tag{5}$$

$$(-CH_2) + CO_2 \rightarrow 2CO + H_2. \tag{6}$$

(i) *Air gasification*: Air gasification is most widely used technology as single product is formed at high efficiency and with out requiring oxygen. A low heating value gas is produced containing up to 60% N_2 having a typical heating value of 4–6 MJ/Nm^3 with byproducts such as water, CO_2, hydrocarbons, tar, and nitrogen gas. The reactor temperature of 900–1100 °C was achieved.

(ii) *Oxygen gasification*: Yields a better quality gas of heating value of 10–15 MJ/Nm^3. In this process relatively a temperature of 1000–1400 °C is achieved. But it requires an O_2 supply with simultaneous problem of cost and safety.

(iii) *Steam gasification*: Biomass steam gasification results in the conversion of carbonaceous material to permanent gases (H_2CO, CO_2, CH_4 and light hydrocarbons), char and tar. To avoid corrosion problems, poisoning of catalysts and to improve the overall efficiency of the gasification process, tar components needs to be minimized [20].

Andersson and Harvey (Sweden, 2006) described two alternative options for the production of hydrogen as follows:

1. Pulp-mill-integrated hydrogen production from gasified back liquor.
2. Stand-alone production of hydrogen from gasified biomass.

The comparison assumes that the same amount of biomass that is imported in option 1, is supplied to a stand-alone hydrogen production plant and that is gasified black liquor in option 2, is used in a black liquor gasification combined cycle (BLGCC) CHP unit. The comparison is based upon equal amounts of black liquor fed to the gasifier, and identical steam and power requirements for the pulp mill. The two systems are compared on the basis of total CO_2 emission consequences, based upon different assumptions for the reference energy system that reflects different societal CO_2 emissions reduction target levels. Authors have reported that the hydrogen production from gasified black liquor (option 1) is best from a CO_2 emissions' perspective. Whereas, with high CO_2 emissions associated with electricity production, hydrogen from gasified biomass and electricity from gasified black liquor (option 2) is preferable [21].

Meng et al. have also overviewed alternative thermo-chemical (pyrolysis and gasification) and biological (bio-photolysis, water–gas shift reaction and fermentation) technologies for hydrogen production from biomass. In their overview the authors have concluded that the thermo-chemical pyrolysis and gasification hydrogen production methods are economically viable and are likely to become competitive with the conventional natural gas reforming method [22].

Co-gasification of coal mixed with bagasse waste was found to be feasible by Andre (2005, Portugal) et al. [23]. The gasification experiments were conducted in a fluidized bed gasifier and the results indicate that increase in bagasse content increased tars and gaseous

hydrocarbons. This was reduced by increasing the bed temperature and air flow rate. An increase in the temperature up to 885 °C, achieved 45% of hydrogen yields (Table 11). A reduction of around 30% in gaseous hydrocarbons was also achieved by raising O_2/fuel ratio to 0.6 g/g daf [23].

Steam reforming of the bio-oil obtained from fast pyrolysis is an important process for the production of hydrogen. Riochee and coworkers (2005, Ireland) have worked on the development of an efficient catalyst for steam reforming process so as to overcome the problems of complex chemical structure of reactants. The steam reforming of the model compounds was investigated in the temperature range of 650–950 °C over Pt, Pd and Rh supported on alumina and a Ceria–Zirconia sample. The model compounds used were acetic acid, phenol, acetone and ethanol. Results from Table 12 indicate that the nature of the support appeared to play a significant role in the activity of these catalysts.

The use of Ceria–Zirconia and Redox mixed oxide leads to higher hydrogen yields as compared to the case of the alumina-supported catalysts. The supported Rh and Pt catalysts were the most active for the steam reforming of these compounds, while Pd-based catalysts poorly performed. The activity of the promising Pt and Rh catalysts was also investigated for the steam reforming of a bio-oil obtained from beech-wood using fast pyrolysis process. Temperatures close around, or higher than 800 °C were required to achieve significant conversions to CO_x and H_2 (e.g., hydrogen yields around 70%) [24].

Air blown gasification of biomass was carried out by Zhang (2005, China) et al. Authors have suggested that the concentration of hydrogen obtained by this process is relatively low (about 8.0%). Steam reforming of tars and light hydrocarbons and reacting steam with carbon monoxide via the water–gas shift reaction can increase hydrogen content (almost 30 vol%). Experiments were conducted with temperature, space velocity and steam/gas

Table 11
Hydrogen concentration with temperature

Temperature (°C)	Hydrogen concentration (%v/v)
765	30
815	34
845	38
885	44

Table 12
Activity of various catalysts used for steam reforming of model compounds

Catalyst	Hydrogen yields (%)			
	Acetic acid	Acetone	Ethanol	Phenol
1% Pt–Al_2O_3	20–40	20–40	20–40	>80
1% Rh–Al_2O_3	40–60	60–80	60–80	>80
1% Pd–Al_2O_3	20–40	20–40	40–60	20–40
1% Pt–$CeZrO_2$	60–80	60–80	40–60	>80
1% Rh–$CeZrO_2$	60–80	60–80	60–80	>80
1% Pd–$CeZrO_2$	40–60	40–60	20–40	>80

ratio as the variables in a pilot-scale fluidized bed reactor located at the Biomass Energy Conversion Facility (BECON) in Nevada [25].

Lv Pengmei et al. (2003, China) and Jingxu Chen (Canada) have performed a series of experiments of biomass air-steam gasification in a fluidized bed reactor [26]. During their experiments the gasifying agent, air, was supplied into the reactor from the bottom whereas steam was added from a point above the biomass feeding location. Pine dust of different mesh sizes, i.e., of 0.6–0.9, 0.45–0.6, 0.3–0.45, and 0.2–0.3 mm was chosen as the feed stock. Results from Table 13, highlight that yields of hydrogen increases with the increase in the temperature. The highest hydrogen yields of 71.0 g H_2/kg biomass were obtained at a reactor temperature of 900 °C, equivalence ratio of 0.22 and steam to biomass ratio of 2.70 [26].

Dasappa et al. (India, 2004) have reported a state of the art technology of open top re-burn down draft gasifier for biomass gasification system coupled with the internal combustion engine or thermal device. The gasification system has proved a reliable alternative for rural electrification and industrial operations meeting thermal and electrical needs [27].

Filippis et al. (Italy, 2004) have also proposed the construction of a two stage gasification reactor for bagasse gasification. The group has also conducted different bench scale experiments using Cuban bagasse. The results obtained from bench scale gasification experiments indicate that this reactor allows a complete gasification of biomass avoiding the formation and tar. In addition, the use of a nickel catalyst makes the composition of outgoing syngas close to that predicted at the equilibrium conditions [28].

Perez et al. (Spain, 1997) have carried out experiments and have described different methods for cleaning the gas obtained from the biomass gasification. The gas obtained from the gasification process do require some cleaning for further applications as it comprises tars and dusts (which include char, coke, and fine particles of sand, etc.). To improve the quality of the product the authors have also conducted bench scale experiments in a bubbling fluidized bed reactor. Gasification was achieved at 800–850 °C under atmospheric pressure in the presence of steam. Gas cleaning was carried out by a process called 'hot gas cleaning' wherein ceramic filters were used for the removal of dust. The tar content was removed using catalytic reactors in which catalysts like calcined dolomites and steam reforming (nickel based) catalysts were used [29].

Kim (Columbia, 2002) has conducted gasification of carbonaceous liquid wastes such as waste oil or waste organic solvents and solid carbonaceous waste such as coal and shredded waste tire or waste oil into CO and hydrogen gas. The method comprises the steps of supplying syngas and oxygen gas into syngas burners of the gasification reactors to produce steam and carbon dioxide gas, which in turn reacts the organic materials fed into

Table 13
Hydrogen yields with temperature variation

Temperature (°C)	Hydrogen yields (hydrogen per kg biomass, wet basis)
700	22
750	31
800	52
850	64
900	71

the reactor to produce syngas. This method facilitates the control of uniform temperature in gasification reactor as well as produces syngas of high quality by increasing the concentration [30].

Hanaoka et al. have conducted experiments for hydrogen production from woody biomass by steam gasification using a CO_2 sorbent. The hydrogen yield and conversion to gas were largely dependent on the reaction pressure, and exhibit maximum value at 0.9 MPa. Japanese oak without bark was chosen as the biomass for the purpose [31].

Kersten and coworkers (The Netherlands) in the year 2003 introduced a novel multistage circulating fluidized bed reactor which prevents the back mixing of gases and solids. This reactor was fabricated in such a manner that it overcomes the drawbacks of the circulating fluidized bed reactor. In the novel reactor it is possible to create oxidation segments in which oxygen gas reacts exclusively with char resulting in an increased carbon conversion and consequently improved gasification efficiency [19].

Comparative studies of gasification of biomass in a fixed bed and a fluidized bed gasifier have been presented by Ragner Warnecke (2000, Germany). Criteria for comparison chosen by the author were technology, use of material, use of energy, environment and economy. An advantage mainly depends on the physical consistency of the inputs. The author has concluded that there is no significant advantage for the fixed bed or the fluidized bed reactor [32].

Coluimba Di Blasi and team (Italy, 1999) have studied gasification characteristics of several biomasses on a laboratory scale countercurrent fixed bed gasification plant. Experiments were carried out to produce data for process modelling and to compare the gasification characteristics of different biomass. Results from Table 14 indicate that gas yield increases with the increase in the temperature [12].

Narvaez and coworkers, during the year 1996 (Spain) performed various biomass gasification reactions with air in bubbling fluidized bed gasifier. Reactions were carried out in the temperature range of 750–850 °C. Composition and tar content patterns in the gas were studied with operational parameters. Authors have also studied the effects of gasification variables statistically [33].

Biomass wastes obtained from cleaning of forests and from agricultural and industrial activities were used for the experiments conducted by Franco et al. (2002, Portugal). Steam gasification studies were carried out in an atmospheric fluidized bed operated over a temperature range of 700–900 °C. Three types of biomass were studied, i.e., *Pinus pinaster*,

Table 14
Yields of gas produced with hydrogen

Temperature (K)	Gas yield (wt% mf)
540	6
600	9
625	14
650	15
675	16
700	17
750	17
775	17
800	18
840	19

Table 15
Hydrogen gas yields of different biomass with temperature

Temperature (°C)	Hydrogen gas yields (mol%)		
	Pine waste	Holm oak	Eucalyptus
750	27	36	23
800	32	33	27
840	30	35	36
890	33	45	43

Eucalyptus globules and holm-oak. The operating conditions were optimized for a gasification temperature of 830 °C and steam/biomass ratio of 0.6–0.7 w/w. Table 15 shows the results of yields of hydrogen with temperature produced from the different feedstock [34].

Air gasification of agricultural residues like almond shells and wood at high temperature was carried out by De Bari and others (Italy) in the year 1999. A small-scale fixed bed downdraft gasification plant coupled with a reciprocated internal combustion engine was used by the author. Authors have provided detailed information of the organics and inorganic composition of the flue gas. A different feedstock composition was found to be associated with the some important variations in the process monitored parameters such as gasification rate, the tar content and the char yield in the flue gas [35].

4.5. Steam gasification of char

4.5.1. Char from fast pyrolysis system

Some reasonable amount of char is produced during the fast pyrolysis of biomass. This char is highly reactive and can be gasified with gasifying agents such as steam, CO_2, oxygen and H_2 to gaseous fuels. Recently there is lot of interest in utilizing the pyrolysis-derived char for steam gasification to produce gaseous fuel.

The composition of the gas produced during steam gasification of the char depends on the inherent nature of the char and the process conditions employed during steam gasification.

The steam gasification experiments were carried out in a down flow reactor [36]. It consists of a pre-heater to vaporize water into steam, an inconell reactor (450 mm long and 11 mm i.d.) with temperature controller, a metering pump, a liquid collection trap, and a gas collection system.

Bakshi and associates (1999) (Canada) performed steam gasification of lignin, biomass chars and Westvaco Kraft Lignin to hydrogen and high and medium bitumen gas. Three lignins Kraft-1, Kraft-2 and Alcell were gasified at 600–800 °C in a fixed bed with steam flow rate of 10 g/h/g of lignin. Hydrogen contents ranged from 30 to 50% [37].

5. Hydrogen as "automotive fuel"

The possibility of using H_2 as automotive fuel has received attention because of the increased importance of reducing exhaust emissions. When an IC engine uses pure H_2, the equivalence ratio can be extended to very low values, where exhaust emissions are reduced

by several orders of magnitude. Another advantage of hydrogen engine is that it does not generate carbon-dioxide, carbon mono-oxide, hydrocarbons, lead or S pollutants. Also using gaseous hydrogen, overcomes the problems of fuel atomization and vaporization. With air, engine produces NO_x which can be controlled in hydrogen engines by running it very lean, thus lowering the temperature and lowering the engine rpm allowing better heat dissipation. H_2 can be considered more thermally efficient than gasoline as it burns better in excess air. On an average of hydrogen vehicles are 22% more efficient.

Koroneos et al. have carried out investigation studies on environmental aspects of petroleum based aviation fuel. Due to high energy content, combustion kinetics and absence of carbon dioxide hydrogen is considered as a future aviation fuel. Production of hydrogen from renewable energy sources has significantly lower environmental impact as compared to that of petroleum fuels [38].

6. Conclusions

Visualizing the present worldwide scenario of the energy requirements and the concerned pollution, there is an utmost need of an alternative fuel source. This fuel should not only be a potential substitute for the depleting fossil fuels but also should cause least harm to the environment. Hydrogen could be a potential fuel which can meet both the requirements.

There are various thermo-chemical conversion technologies which can be applied for conversion of renewable biomass into hydrogen rich gas. As literature suggests thermo-chemical process like pyrolysis followed by reforming of bio-oil and gasification has received significant amount of interest as these provide improved quality fuel product.

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